
(12) **UK Patent Application** (19) **GB** (11) **2 010 287 A**

- (21) Application No. **7845643**
(22) Date of filing **22 Nov 1978**
(23) Claims filed **22 Nov 1978**
(30) Priority data
(31) **49343/77**
(32) **28 Nov 1977**
(33) **United Kingdom (GB)**
(43) Application published
27 Jun 1979
(51) **INT CL²**
C08K 9/06 5/05
C08L 71/02
(52) Domestic classification
C3K 111 120 201 230 262
291 292 GA
(56) Documents cited
GB 1502840
GB 1499721
GB 1405551
GB 1392763
GB 1346951
GB 1304757
GB 1286842
GB 1278808
GB 1262470
GB 1252052
GB 1210098
GB 1025913
GB 954574
(58) Field of search
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C3L
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(54) Stabilized silane-treated fillers

(57) Filler compositions comprising a siliceous filler (especially silica) and a silylated coupling agent, together with polar compound such as a polyether (e.g. a condensate of polyethylene oxide) or an aliphatic polyhydroxy compound (e.g. glycerol) as stabiliser, are useful particularly as masterbatches, for mixing with more filler before or during use in a polymer, especially a vulcanisable elastomer.

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SPECIFICATION

Stabilised siliceous filler compositions and their use in polymers, especially vulcanisable elastomers

5 This invention relates to improved siliceous filler compositions.

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Compositions have been proposed which comprise a particulate siliceous filler mixed with an organo-silicon compound which is capable of coupling to the filler and which is preferably also capable of reacting with a polymer. Such compositions are particularly suitable for mixing with a polymer to form a polymer composition (especially a rubber composition) because the presence of the organo-silicon compound leads to an improvement in certain properties of the polymer composition in comparison with the properties of a polymer composition which contains a siliceous filler but which does not contain an organo-silicon compound.

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It is desirable to be able to form a so-called "master-batch" of mixed siliceous filler and organo-silicon compound, which contains a proportion of organo-silicon compound to siliceous filler which is greater than the proportion required when the siliceous filler composition is incorporated into the polymer composition.

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The "master-batch" siliceous filler composition may be mixed with further siliceous filler so as to provide a proportion of organo-silicon compound to siliceous filler which is desired in the polymer composition. This may be done before, during, or after incorporating the master batch into the polymer composition. We find, however, that using a master-batch and diluting it with further siliceous filler suffers from a disadvantage when the master-batch has been stored for some time. Thus, certain properties of the resultant polymer composition (and, in particular, tensile modulus properties) are inferior to the properties of a polymer composition which incorporates a siliceous filler and an organo-silicon compound freshly mixed in the proportions desired, either (a) by mixing the polymer with the siliceous filler and with the organo-silicon compound or (b) by mixing the polymer with a siliceous filler composition which has itself been made by directly mixing siliceous filler and organo-silicon compound in the proportions desired in the polymer composition.

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We have now found a way of overcoming the aforementioned disadvantage.

The present invention provides a filler composition comprising:-

- 30 (A) an organo-silicon compound containing at least one group which is capable of reacting with a siliceous filler and at least one non-hydrolysable organic group attached directly or indirectly to Si,
- (B) an organic stabiliser component as hereinafter defined which is capable of associating with the surface of a siliceous filler, and
- (C) a finely divided particulate siliceous filler.

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35 We find the presence of the organic stabiliser component B in the filler composition enables the composition to be stored for prolonged periods of time, and subsequently to be mixed with a polymer and with further siliceous filler in an amount to give the desired proportion of organo-silicon compound to siliceous filler, with little or no adverse affect on the properties of the resultant polymer composition.

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Our invention is especially applicable to master-batches which are to be used in conjunction with additional filler, but can also be applied to stabilise mixtures to which no further filler need be added.

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The organo-silicon compound is suitable a compound containing at least one group - Si(X)_n where X (which may be the same or different) is H, OH or OR, where R is a hydrocarbon or substituted hydrocarbon group, and n is 1, 2 or 3. Preferred organo-silicon compounds are those which contain at least one group OR. R is preferably a lower alkyl group, for example an alkyl group containing from 1 to 4 carbon atoms, i.e. methyl, ethyl, propyl or butyl. R may bear substituent groups, in which case it is preferred that the substituents be neither acidic nor basic in nature. Further preferred organo-silicon compounds are those containing the group - Si(OR)_nY_{3-n} wherein R has the meaning given above and Y represents a hydrocarbon substituent, especially a lower alkyl group of 1 to 4 carbon atoms. The organo-silicon compound may contain more than one group - Si(X)_n or - Si(OR)_nY_{3-n}, which may be the same or different.

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50 The non-hydrolysable organic group attached to silicon in the organo-silicon compound is preferably capable of reacting with the polymer in the polymer composition. For example, this organic group may contain unsaturation, especially ethylenic unsaturation, and it is suitably derived from a polymeric molecule. Where the filler composition of the invention is to be incorporated into a curable rubber composition it is especially convenient for the non-hydrolysable organic group to contain at least one ethylenically unsaturated hydrocarbon group which is capable of taking part in the rubber-curing reaction. Thus, the non-hydrolysable organic group may be part of a polydiene structure. Examples of polydiene structures are those of polymers and copolymers derived from one or more dienes, of which the most conveniently available is butadiene, although others may be used if desired (for example isoprene and chloroprene and mixtures thereof). Examples of other compounds which may be copolymerised with the diene or dienes include a wide range of vinyl monomers, for example, styrene, acrylonitrile, and mixtures thereof.

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The non-hydrolysable organic group in the organo-silicon compound may contain sulphur. This is particularly convenient where the filler composition of the invention is to be incorporated in a sulphur-curable rubber composition, because the sulphur in the organo-silicon compound may take part in the curing reaction and provide a link between the organo-silicon compound and the rubber.

65 The non-hydrolysable organic group in the organo-silicon compound is preferably one which has a

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molecular weight in the range up to 500,000. Where the organic group is a polymer it preferably has a molecular weight in the range 200 to 50,000, especially in the range 1000 to 10,000. The non-hydrolysable organic group may be attached directly or indirectly to the silicon atom or atoms.

The term "non-hydrolysable" is used in the sense of meaning that the group as a whole is not removed from the silicon by hydrolysis.

Examples of organo-silicon compounds which may be used in the composition of our invention include:

(a) Compounds comprising an organic molecular chain structure bearing at least one mono-alkoxy or di-alkoxy silyl group or corresponding substituted alkoxy or di-alkoxy silyl groups. These compounds may most conveniently have an organic molecular chain structure derived from a polydiene (for example a polybutadiene) and may be made by known silylating methods, for example by reaction of a polydiene with a hydrosilane containing the silyl group which it is desired to introduce into the molecule (conveniently in the presence of a catalyst, for example a platinum-containing catalyst).

(b) Compounds comprising an organic molecular chain structure bearing at least one tri-alkoxy-silyl group. Most conveniently these may have an organic molecular chain structure derived from a polydiene, for example polybutadiene. Such compounds are included among the many contained within the definitions in US Patent No 3759869 of Skeist.

(c) Compounds containing a mono-alkoxy, di-alkoxy or tri-alkoxy silyl group attached, by way of a short organic chain, to a sulphur-bearing group which may be for example a sulphhydryl group (SH), a polysulphide group or the like. An example of this latter type of organo-silicon compound is a compound having the structure $\text{HS}(\text{CH}_2)_n\text{Si}(\text{OR})_3$ where n is an integer (conveniently an integer in the range 2 to 10, for example 3) and R is a hydrocarbon or substituted hydrocarbon group, for example a lower alkyl group containing from 1 to 4 carbon atoms, for example methyl or ethyl. A further example is a compound having the structure



where n and R have the meanings indicated above, and x is at least 2, e.g. 2 to 4 or even higher.

Specific examples of such compounds are bis-(gamma-triethoxysilyl propyl) tetrasulphide and gamma-mercapto- propyl trimethoxy silane.

The number of silicon atoms in the organo-silicon compound is preferably such as to provide at least one silicon atom for each 3000 of the molecular weight of the non-hydrolysable organic group.

The organic stabiliser component B in the filler composition of the invention (an organic compound capable of associating with the surface of a siliceous filler) is a compound which contains at least one polar group. Suitable polar groups include ether oxygen atoms, amino nitrogen atoms (including those with and without a substituent on the nitrogen atom), hydroxyls, and ketone groups. The number of such polar groups in the organic compound may vary, but it may be as low as in the range 1 to 16, but may be much higher, for example up to 100 or even more. The optimum number may depend on the nature of the organo-silicon compound, and, where the latter compound contains a group $-\text{Si}(\text{X})_n$, on the value of n.

Very effective results are obtained when the stabiliser component B is a polyether compounds. Especially useful polyether compounds are substantially linear polyethers. The most convenient examples of such compounds are the polymers and copolymers of alkylene oxides, for example those derived from ethylene oxide and/or propylene oxide. Such polymers, sometimes called polyethylene glycols or propylene glycols, or even just "polyethers", may optionally have an organic end group etherifying one or both of the terminal oxygen atoms of the molecule. The molecular weight of the polymer compounds is preferred to be in the range 106 to 10,000, though higher and lower molecular weights may be used if desired.

Diethylene glycol and several polyethylene glycols are especially useful additives for this purpose, as they are well known to be useful in rubber compounding and therefore have no troublesome side-effects in the final product.

Copolymers of ethylene oxide and/or propylene oxide which may also be mentioned include the condensates of the alkylene oxides (especially ethylene oxide) with a variety of organic compounds, (especially an organic hydroxy compound) for example alcohols (especially aliphatic higher fatty alcohols of 8 to 20 carbons), phenols and alkylated phenols, aliphatic carboxylic acids, aliphatic carboxylic amides, and mixtures thereof. Many such products are available in commerce as surfactants or dispersants.

Another useful group of polar compounds comprises aliphatic poly-hydroxy compounds, especially those which are liquid and of molecular weight up to about 300. Examples of these include glycerol and hexane-triol.

The finely-divided particulate siliceous filler for use in the compositions of the invention may have any form conventional in the art as suitable for a filler, may have a wide variety of particle shapes and sizes, and may be of natural or synthetic origin. Thus, the filler may, for example have an average particle diameter less than 100 nm or a specific surface area greater than 25 m² per gram, though we prefer that the average particle diameter should be in the range 40 Angstrom to 1000 Angstrom, for example about 200 Angstrom.

Most commonly the filler will be of a substantially spherical shape, though it may if desired be of fibrillar or laminar form, for example the residual pseudomorphs remaining after silicate minerals (for example vermiculite, chrysotile asbestos and the like) are dispersed and treated with acids to remove

cations.

Most conveniently the filler is in the form of a finely divided, free-flowing powder, and this is the form in which such materials are usually available in commerce. The filler may be dried, for example by heat, before use in the compositions of our invention, in order to drive off all or part of adsorbed water.

5 Chemically, suitable siliceous filler particles may consist of substantially pure silica or may contain silica together with a proportion of one or more other metal oxides, for example acidic oxides, eg titania, or metal oxides capable of forming silicates, eg calcium, magnesium, aluminium and combinations of these. They may consist of a silicate, provided the silicate is one which is suitable for use as a filler, for example if it is insoluble in water. Suitable silicates include clays which can be produced in a sufficiently

10 finely divided form to serve as fillers.

We strongly prefer that the siliceous particles contain free silanol groups at their surface, either by virtue of their constitution or by modification during manufacture of the material into particles of desired dimensions. We therefore prefer that the siliceous particles consist predominantly of silica and we especially prefer that they consist of substantially pure silica itself. A very suitable material is that known as

15 precipitated silica, which may be made for example by precipitating silica from aqueous solutions of alkali metal silicates by acidification. If desired, other forms of silica may be used, for example that made during burning silicon tetrachloride in air (commonly described as "fumed silica").

The proportions of the components of the filler composition of the invention may vary but they are usually in the range:-

20 (a) 5 to 150 parts by weight of organo-silicon compound for every 100 parts by weight of the siliceous filler, and

(b) 1 to 60 parts by weight of organic stabiliser component capable of associating with the surface of a siliceous filler for every 100 parts by weight of the siliceous filler.

In order that use of the organic stabiliser component B should result in a substantial advantageous effect it is preferred that the latter be present in the composition in a proportion of at least 5 parts by weight for every 100 parts by weight of organo-silicon compound, and preferably in a proportion in the range 10 to 50 parts by weight for every 100 parts by weight of organo-silicon compound.

The optimum proportions of the components of the composition is best determined by simple trial, and we prefer to use sufficient of the filler to result in the composition being a free-flowing powder. The mode of mixing of the components may need to be adapted to suit the particular components used, for example a high-shear blender may be most suitable and it may be helpful to apply some heat. Especially convenient is the use of a solvent to assist the dispersion of the organic materials (components A and B) over the particulate filler C; a suitable solvent for this is the solvent which may have been used for carrying out the preparation of the organo-silicon compound. Thus it is preferred to make the organo-silicon compound in an organic solvent, dissolve the organic stabiliser component B in the resulting solution, and then mix the solution with filler and evaporate off the solvent.

Alternatively, the components of the composition may be mixed in a suitable blender, eg in a ball mill. This may be done in the absence or in the presence of a solvent.

Although some reaction of the organo-silicon compound with the siliceous filler may take place during the production of the composition of the invention it is preferred that the extent of reaction be kept to a minimum. The conditions used in the blending of the components of the composition, and especially the temperature used, should be chosen with care so as to minimise the extent of premature reaction.

The composition of the invention may contain other components, for example, one or more antioxidants. The proportions of antioxidant may suitably be in the range 0.1 to 5 parts by weight of antioxidant for every 100 parts by weight of organo-silicon compound.

In a further embodiment of the present invention there is provided a polymer composition comprising at least one organic polymer and a filler composition as hereinbefore described. The polymer composition suitably comprises at least 0.4 part by weight of the filler composition as hereinbefore described. The polymer composition suitably comprises at least 0.4 part by weight of the filler composition for every 100 parts by weight of the organic polymer, and preferably 2 to 40 parts by weight of the filler composition for every 100 parts by weight of the organic polymer.

The polymer composition may be produced by blending the organic polymer and the filler composition by known methods, for example, by using a ball mill, and especially in the case where the organic polymer is a rubber, by using a multi-roll mill, eg a twin-roll mill. The polymer composition may also include additional siliceous filler in an amount chosen to achieve a proportion of organo-silicon for example, from 1 to 20 parts by weight of organo-silicon compound for every 100 parts by weight of siliceous filler, which is desired in the polymer composition. This additional siliceous filler in the polymer composition may be the same as the siliceous filler in the filler composition, but it may be different if desired.

The polymer composition suitably contains a total of from 1 to 150 parts by weight siliceous filler for every 100 parts by weight of organic polymer.

The organic polymer may be a thermoplastic organic polymer, for example:-

a polyolefin, eg polyethylene, polypropylene or an olefin copolymer;

an acrylic polymer, eg poly(methyl methacrylate);

a halogen-containing polymer, eg poly(vinyl chloride) or poly(vinylidene chloride).

65 Advantageously, the polymer may be a curable (especially vulcanisable) polymer and preferably an

elastomer.

The organic polymer is preferably caused to react with the non-hydrolysable organic group in the organo-silicon compound, for example by including a free-radical generator in the polymer composition and by heating the composition to cause reaction. In order that reaction may readily be effected it is preferred that the non-hydrolysable organic group in the organo-silicon compound contains ethylenic unsaturation. Alternatively, where the organic polymer is a sulphur-curable rubber the non-hydrolysable organic group in the organo-silicon compound may contain one or more sulphur atoms which may take part in the curing reaction and provide a link between the organo-silicon compound and the rubber.

Where the organic polymer is a curable rubber it may be a natural or synthetic rubber, for example, a polymer containing polymerised diene units, for example polymerised butadiene, isoprene or chloroprene. The diene may be copolymerised with each other and/or with non-dienes. Suitable rubbers include polybutadiene, polyisoprene, polychloroprene, acrylonitrile-butadiene rubbers, and styrene-butadiene rubbers. The polymer composition may contain materials conventional in the rubber curing art, for example, sulphur and accelerators. Under the conditions conventionally used for curing the rubber it will generally be found that where the non-hydrolysable organic group of the organo-silicon compound contains unsaturation or contains sulphur it will react with the rubber molecule, especially in the presence of conventional rubber-curing materials. Also the conditions of the rubber curing reaction will generally be such as to cause reaction between the siliceous filler and the organo-silicon compound.

The testing or demonstration of the stabilising efficiency of the organic stabilising component can be shown by several different tests. The actual effect in making a final polymer composition is most direct evidence, but we find that an excellent test comprises subjecting a mixture of the organo-silicon compound, the filler and the stabiliser to standard conditions of temperature and humidity, and measuring the evolution of alkanol (eg ethanol) when the organo-silicon compound contains alkoxy groups. The composition will evolve alkanol very much less rapidly in the presence of the stabiliser. This test is described more fully as follows:-

1 part by weight of siliceous filler to be used in the composition of the invention is mixed with 1 part by weight of an organo-silicon compound (for example a diethoxy methyl silyl polybutadiene containing on average 1 atom of silicon for every 10 molecules of butadiene) and the mixture is placed in a closed container containing air at 35% relative humidity at a temperature of 25°C and the amount of ethanol released in 24 hours is measured, eg by gas-liquid chromatography. The release of ethanol indicates reaction between the organo-silicon compound and the siliceous filler. 0.4 part by weight of organic compound under test is then mixed with 1 part by weight of siliceous filler, the mixture is then mixed with 1 part by weight of the diethoxy methyl silyl polybutadiene, the resultant mixture is placed in a closed container containing air at 35% relative humidity at a temperature of 25°C, and the amount of ethanol released in 24 hours is measured. A preferred organic compound suitable for use in the filler composition of the present invention is a compound which reduces the amount of ethanol released in 24 hours to one tenth or less of that which is released in the absence of the organic compound.

An alternative test, which correlates well with the one already described, comprises maintaining the composition under simulated storage conditions (standard temperature and humidity) for a period and then measuring the loss of solubility of the organo-silicon compound component. A suitable solvent for this test is toluene or methanol, and the more efficient the stabiliser is, then the smaller will be the amount of organo-silicon compound which cannot be recovered from the mixture by extraction.

The invention is illustrated by the following Examples in which all parts and percentages are expressed by weight unless otherwise stated.

EXAMPLE 1

1 part of a commercially available grade of precipitated silica filler, containing 0.7% sodium ions and 0.7% alumina calculated on the dried material, was mixed with 0.48 parts of diethylene glycol and to this mixture 1 part of polybutadiene silicate* was added. The components of the mixture were thoroughly blended by ball-milling the mixture for 2 hours to produce a fine particle size product which will be referred to as the masterbatch.

(*The polybutadiene silicate was prepared by reacting 13.4 parts of methyl diethoxy silane with 54 parts of polybutadiene (48% 1:2, 52% 1:4) of molecular weight 3000 in toluene for 1 hour at 90 to 100°C in the presence of chloroplatinic acid catalyst. The toluene was subsequently evaporated and the polybutadiene silicate was recovered in the form of an oil).

Immediately after preparation of the masterbatch 15.6 parts of the masterbatch were blended on a mill with 100 parts of styrene-butadiene rubber (SBR 1509) and then the following components were added in the order stated,

0.8 parts of 'Vulcafor' M BTS (mercaptobenzthiazole),
1.2 parts of 'Vulcafor DPG' (diphenylguanidine),
2 parts of zinc oxide,
2 parts of stearic acid,
0.5 parts of triethanolamine,
43.6 parts of precipitated silica, and
2.5 parts of sulphur.

The rubber composition was thoroughly blended on the twin-roll mill.

Sheets of the rubber composition were then cured by heating in a hydraulic press at a temperature of 160°C for 8 minutes and the tensile properties of the resultant sheets were measured. The results are given in Table 1. In a further experiment the above described procedure was followed to produce a cured rubber composition except that the master batch was blended with the styrene-butadiene rubber and with other components of the rubber composition 37 days after the preparation of the master batch. The tensile properties of the cured rubber sheets are given in Table 1.

By way of comparison a master batch was prepared from a mixture of 1 part of polybutadiene silicate and 1 part of precipitated silica by ball-milling the mixture for 2 hours. The diethylene glycol was omitted.

In a first comparative experiment the master batch was blended immediately after its preparation with a styrene-butadiene rubber and with the other components of the rubber composition following the above described procedure, and in addition with 3 parts of diethylene glycol, and sheets of the rubber composition were cured by heating in a hydraulic press at a temperature of 160°C for 8 minutes and the tensile properties of the resultant sheets were measured. The results are given in Table 1.

In a second comparative experiment the master batch prepared from polybutadiene silicated and precipitated silica was allowed to stand for 37 days and the blended with the other components of the rubber composition following the procedure described above in the first comparative experiment. The properties of the sheets prepared by heating the sheets in a hydraulic press at a temperature of 160°C for 8 minutes are given in Table 1.

It can be seen that the master batch which contains diethylene glycol, when allowed to stand for 37 days before use and then incorporated in a rubber results in superior tensile modulus properties than does a master batch which was prepared in the absence of diethylene glycol and which had also been allowed to stand for 37 days before use.

Table 1

Time from preparation of master batch days	Properties of cured rubber sheet	Experiment Master batch-precipitated silica-diethylene glycol polybutadiene silicate	Comparison Master batch-precipitated silica-polybutadiene
0	Tensile Strength MN/m ²	9.2	8.8
	Elongation or break %	350	340
35	Tensile modulus 100% MN/m ²	3.3	3.3
	Tensile modulus 200% MN/m ²	5.4	5.4
	Tensile modulus 300% MN/m ²	7.9	7.9
37	Tensile strength MN/m ²	9.8	10.0
40	Elongation at break %	320	390
	Tensile modulus 100% MN/m ²	3.9	3.2
	Tensile modulus 200% MN/m ²	6.4	5.2
	Tensile modulus 300% MN/m ²	9.4	7.8

EXAMPLE 2

Masterbatches were prepared by mixing 1 part of a commercially available precipitated silica filler (as specified in Example 1) with 1 part of bis-(gamma-triethoxy silylpropyl) tetrasulphide and 0.4 part of a stabiliser.

The stabilisers used were:

Masterbatch A: Polyethylene glycol, molecular weight 380-420 ("PEG 400")

Masterbatch B: Polyethylene glycol, molecular weight 3800-4800 ("PEG 4000")

Masterbatch C: Polyethylene glycol, molecular weight 950-1050 ("PEG 1000") (50%) plus a condensate of mixed cetyl and oleyl alcohols with about 8 molecular proportions of ethylene oxide (50%).

Masterbatch D: No stabiliser (for purposes of comparison).

The silane compound and the stabilisers were mixed together and then stirred into the silica, and thoroughly mixed by ball-milling for 1 hour to produce a product of small particle size. In the case of masterbatch C, 2.5 parts of toluene were added to assist homogeneity and finally removed by evaporation at 30 to 50°C.

These masterbatches were then exposed, in shallow trays, to "tropical humidity conditions" (38°C and 90% relative humidity) for seven days. They were then used to prepare silica-filled rubber vulcanisates, whose cure and tensile properties were then measured by established methods.

The rubber formulations used were as follows, in which it is to be noted that further amounts of the stabiliser components are added because these are of a type known to have beneficial effects in silica-filled rubber formulations and it was desired to make the pairs of compositions properly comparable.

Ingredients	Rubber Mixes						
	1	2	3	4	5	6	
5 Rubber SBR 1509	100	100	100	100	100	100	5
Silica Filler	48	48	48	48	48	48	
"Ultrasil" VN3							
Zinc Oxide	2	2	2	2	2	2	
10 Stearic acid	2	2	2	2	2	2	10
Mercaptobenzthiazole	0.8	0.8	0.8	0.8	0.8	0.8	
Diphenylguanidine	1.2	1.2	1.2	1.2	1.2	1.2	
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	
15 Masterbatch A	4.8	—	—	—	—	—	15
Masterbatch D	—	4.0	—	—	—	—	
"PEG 400"	1.2	2.0	—	—	—	—	
20 Masterbatch B	—	—	4.8	—	—	—	20
Masterbatch D	—	—	—	4.0	—	—	
"PEG 4000"	—	—	1.2	2.0	—	—	
25 Masterbatch C	—	—	—	—	4.8	—	25
Masterbatch D	—	—	—	—	—	4.0	
"PEG 1000"	—	—	—	—	1.6	2.0	
Condensate of cetyl/oleyl alcohols with 8 mol ethylene oxide	—	—	—	—	—	0.4	
30 Minimum Viscosity	9	10	9	10.5	8	10	30
Induction Time (minutes)	2.4	2.3	2.4	2.3	2.0	2.4	
Peak Cure State	100	102	94	90	97	94	
95% Cure	95.4	97.4	89.7	86.1	92.6	89.8	
35 Time to 95% Peak	9.5	9.5	11.0	9.3	10.3	8	35
Cure time (160°C)	10	10	11.5	9.7	10.8	8.5	
40 Tensile Strength kg/cm ²	160	156	157	148	159	144	40
Elongation to Break %	573	595	577	636	555	638	
Modulus at 300% kg/cm ²	70	66	70	58	73	54	
45 Tear Strength kg/mm	5.4	4.8	4.9	4.9	4.8	4.8	45

These results show that all the stabilised masterbatches produce better vulcanisates than the unstabilised ones.

EXAMPLE 3

Masterbatches of a precipitated silica filler (as sold under the name "Ultrasil" VN3), a silane coupling agent and a stabiliser were made by mixing the silane with the stabiliser, and then with the filler and then ball-milling for 30 minutes. The silane was bis-(gamma-triethoxysilyl propyl) tetrasulphide, and the proportions of stabiliser (in parts per 2 parts of the silane-silica mixture) are listed in the table below.

The masterbatches were then exposed to warm, humid conditions (38°C at 90% relative humidity) in shallow trays for 7 days. Then their stability was measured by determining the weight of material in them which remained extractable by toluene. This was done by stirring them with 100 parts of toluene and then filtering the mixture and evaporating the filtrate to constant weight at 40 to 45°C in a vacuum oven. The weight of extracted material was corrected by deducting the weight of stabiliser used (assuming 100% extraction of the stabiliser) and converted to percentage recovery of the total silane originally present.

Stabiliser	Parts used	% Recovery of silane	
"PEG 400"	0.4	75	
"PEG 400"	0.2)		
5 Condensate of cetyl/oleyl alcohols with 8 mol ethylene oxide	0.2)	84	5
"PEG 1000"	0.4	72	
10 "PEG 4000"	0.4	100	10
Condensate of cetyl/oleyl alcohols with more than 8 mol ethylene oxide	0.4	82	
15 Condensate of cetyl/oleyl alcohols with 8 mol ethylene oxide	0.1	85	15
NONE (for comparison)		43	

EXAMPLE 4

- 20 The procedure of Example 3 was repeated using hexane triol and glycerol respectively as the stabiliser. The solvent used for the extraction test was methanol instead of toluene. The results obtained were: 20

Stabiliser	Parts used	% Recovery of silane	
25 Hexanetriol	0.4	96	25
Glycerol	0.4	83	

EXAMPLE 5

- 30 Masterbatches were prepared by the method described in Example 3, except that the silane used was a polybutadiene silicate (silylated polybutadiene) prepared as described in Example 1 from a polybutadiene of molecular weight 5000 (20% 1:2, 80% 1:4). 30

The stability of the masterbatches was measured by comparing the amounts of ethanol evolved from them and from a corresponding masterbatch containing no stabiliser ingredient.

- 35 The test was carried out by storing a small sample (1.0 gm of unstabilised mix or 1.2 gm of a stabilised mix) in a sealed 1-litre container containing air under ambient conditions. The evolved ethanol was then measured by Gas-Liquid Chromatography (GLC) techniques, and the results are summarised in the table below. The ethanol released is measured in terms of the peak height on the GLC recorder chart. 35

The porportion of the stabiliser used in each case was 0.4 part per 1 part of silica and 1 part of silane.

40 Stabiliser	Ethanol evolved after 25 hours.	40
Condensate of fatty alcohol with ethylene oxide (low proportion)	Less than 1	
45 Condensate of cetyl/oleyl alcohols with ethylene oxide	Less than 1	45
Condensate of monylphenol with 5.5 mol of ethylene oxide	Less than 1	
Condensate of fatty alcohol with ethylene oxide (high proportion)	Less than 1	
50 Condensate of nonylphenol with ethylene oxide (higher than 5.5 mol)	Less than 1	50
NONE (for comparison)		40

55 EXAMPLE 6

Masterbatches were prepared and measured for stability by the methods described in Example 5 except that the silane used was gamma-mercaptopropyl tri-methoxy-silane and the measurements were made to determine evolved methanol. The results were as follows: 55

Stabiliser	Methanol evolution after		
	4 hours	24 hours	
5 Condensate of fatty alcohol with ethylene oxide (low proportion)	310	420	5
"PEG 400"	500	600	
NONE (for comparison)	740	780	
10 (Note: This silane is very reactive, but even so the reduction in methanol evolution is marked).			10

EXAMPLE 7

- Masterbatches were prepared and measured for stability by the methods described in Example 5 except that the silane used was bis-(gamma-triethoxysilyl-propyl) tetrasulphide. They were also repeated using a semi-reinforcing clay filler (HEWP, from English China Clays) of surface area 30 square metres per gram. The results were as follows:

Stabiliser	Ethanol evolution after 24 hours		
	(Silica filler)	(Clay filler)	
20 Condensate of fatty alcohol with ethylene oxide (low proportion)	34	70	
25 "PEG 400"	20	55	25
NONE (for comparison)	74	185	
30 EXAMPLE 8			30

The procedure of Example 1 was repeated, except that a commercially available condensate of a fatty alcohol and ethylene oxide was used in place of the diethylene glycol to prepare the masterbatch, and the polybutadiene silicate was replaced by bis-(gamma-triethoxysilyl propyl) tetrasulphide. The results obtained were:

Days Ageing Under "Tropical Humidity Conditions"	Properties of Cured Rubber Sheet	With Stabiliser		Without Stabiliser	
40	0	Tensile Strength	Kg/cm ² 165	167	40
		Elongation %	689	651	
		Tensile Modulus			
45		100% Kg/cm ²	22	24	
		200% Kg/cm ²	38	40	45
		300% Kg/cm ²	58	62	
50	6	Tensile Strength	Kg/cm ² 155	147	
		Elongation %	656	751	50
		Tensile Modulus			
55		100% Kg/cm ²	22	20	
		200% Kg/cm ²	38	34	
		300% Kg/cm ²	57	49	55
60	42	Tensile Strength	Kg/cm ² 150	117	
		Elongation %	663	858	
		Tensile Modulus			
65		100% Kg/cm ²	25	18	60
		200% Kg/cm ²	41	24	
		300% Kg/cm ²	61	30	

The "Tropical Humidity Conditions" were 38°C and 90% relative humidity.

CLAIMS

1. A filler composition comprising:—
 - (A) an organo-silicon compound containing at least one group which is capable of reacting with a siliceous filler and at least one non-hydrolysable organic group attached directly or indirectly to Silicon,
 - (B) an organic stabiliser component containing at least one polar group and which is capable of associating with the surface of a siliceous filler, and
 - (C) a finely divided particulate siliceous filler.
2. A filler composition as claimed in Claim 1 wherein the organo-silicon compound contains at least one group —OR attached to silicon, in which R represents a hydrocarbon or substituted hydrocarbon group.
3. A filler composition as claimed in Claim 2 wherein the organo-silicon compound contains at least one group —OR attached to silicon, in which R represents an alkyl group of 1 to 4 carbons.
4. A filler composition as claimed in any one of Claims 1 to 3 wherein the organo-silicon compound is derived from an organic polymer of molecular weight in the range 200 to 50,000.
5. A filler composition as claimed in Claim 4 wherein the organo-silicon compound is derived from a polydiene.
6. A filler composition as claimed in any one of Claims 1 to 3 wherein the organo-silicon compound contains sulphur in its structure.
7. A filler composition as claimed in any one of Claims 1 to 6 wherein the organo-silicon compound contains at least one silicon atom for each 3000 of the molecular weight of the non-hydrolysable group.
8. A filler composition as claimed in any one of Claims 1 to 7 wherein the organic stabiliser component B is a polyether.
9. A filler composition as claimed in Claim 8 wherein the polyether is a polymer or copolymer of ethylene oxide or propylene oxide.
10. A filler composition as claimed in Claim 9 wherein the polyether is a condensate of ethylene oxide or propylene oxide with an organic hydroxy compound.
11. A filler composition as claimed in any one of Claims 8 to 10 wherein the polyether has a molecular weight in the range 106 to 10,000.
12. A filler composition as claimed in any one of Claims 1 to 7 wherein the organic stabiliser component is an aliphatic polyhydroxy compound of molecular weight up to about 300.
13. A filler composition as claimed in any one of Claims 1 to 12 wherein the siliceous filler has a particle size in the range 40 to 1000 Angstrom.
14. A filler composition as claimed in Claim 13 wherein the filler is substantially pure silica.
15. A filler composition as claimed in Claim 14 wherein the filler is a precipitated silica.
16. A filler composition as claimed in Claim 13 wherein the filler is a silicate.
17. A filler composition as claimed in any one of Claims 1 to 16 wherein the proportion of organosilicon compound is in the range 5 to 150 parts per 100 parts of filler, by weight.
18. A filler composition as claimed in any one of Claims 1 to 17 wherein the proportion of the stabiliser component is in the range 1 to 60 parts per 100 parts of filler, by weight.
19. A filler composition as claimed in Claim 17 or Claim 18 wherein the proportion of stabiliser component is in the range 10 to 50 parts per 100 parts of organosilicon compound, by weight.
20. Filler compositions substantially as described.
21. Polymer compositions comprising an organic polymer and a filler composition as claimed in any one of Claims 1 to 20.
22. Polymer compositions as claimed in Claim 21 comprising 2 to 40 parts of the filler composition for each 100 parts of the organic polymer.
23. Polymer compositions as claimed in Claim 21 or Claim 22 comprising additional siliceous filler.
24. Polymer compositions as claimed in any one of Claims 21 to 23 comprising a total of from 1 to 150 parts of siliceous filler for each 100 parts of organic polymer, by weight.
25. Polymer compositions as claimed in any one of Claims 21 to 24 comprising 1 to 20 parts of organosilicon compound for each 100 parts of siliceous filler, by weight.
26. Polymer compositions as claimed in any one of Claims 21 to 25 wherein the organic polymer is a vulcanisable elastomer.
27. Polymer compositions substantially as described.

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